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(54) Title: COPOLYMERIZABLE ULTRAVIOLET RADIATION ABSORBING COMPOUNDS AND POLYMERS MADE THEREWITH			
(57) Abstract The invention provides hydroxy-functional cyanoacrylate ultraviolet radiation absorbing compounds. The radiation absorbing compounds can be incorporated into step-growth polymers such as polyurethanes, polyesters, and polycarbonates. The invention also provides such polymers having the radiation compound incorporated therein and articles prepared therefrom.			

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5 **COPOLYMERIZABLE ULTRAVIOLET RADIATION ABSORBING**
 COMPOUNDS AND POLYMERS MADE THEREWITH

Field of the Invention

 This invention relates to novel dihydroxy-functional
 copolymerizable ultraviolet radiation absorbing compounds and polymers
10 prepared therewith. The compounds, which possess at least two primary or
 secondary aliphatic hydroxyl groups, are capable of being reacted into a
 step-growth polymer such as a polyurethane, polyester, or polycarbonate
 polymer.

15 **Background of the Invention**

 Many applications of plastic materials, especially transparent
 materials, involve prolonged exposure to ultraviolet (UV) radiation, which can
 damage or discolor the plastic. A large number of ultraviolet radiation
 absorbing additives are available, but it is well-known that such additives lose
20 their effectiveness over time because of leaching or because of migration to the
 plastic surface.

 To avoid this loss of effectiveness, UV radiation absorbers which
 are capable of being copolymerized into the polymer matrix have been
 developed. Such materials offer the obvious advantage of being incapable of
25 either leaching or blooming, and, thus, maintain their protective function.
 Efforts to date to synthesize such copolymerizable UV absorbers have focused
 on ethylenically-unsaturated molecules, often acrylate-functional molecules,
 which are easily incorporated into acrylate or polyolefin polymers.

 Common core molecules which have received wide-spread
30 attention are esters of 2-cyano-3,3-diaryl acrylic acid, the so-called
 cyanoacrylates. U.S. Patent Nos. 4,218,392; 4,202,834; and 4,129,667;
 (assigned to GAF Corp.) describe acrylate-functional cyanoacrylates. The
 cyanoacrylates described in these patents feature acrylate groups at the terminus
 of the acrylate ester chain which are easily copolymerized with ethylenically-
35 unsaturated monomers such as methyl methacrylate, polyvinyl chloride and
 polyethylene. A common intermediate in the preparation of the GAF
 cyanoacrylates is 2-hydroxyethyl 2-cyano-3,3-diphenylacrylate, a mono-
 hydroxylated cyanoacrylate.

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Patents granted to General Electric Co. (U.S. Patent Nos. 4,366,207; 4,264,719; 4,260,680; and 4,247,475) describe cyanoacrylate-type UV radiation absorbers which are incorporated into polycarbonate polymers via aromatic phenolic hydroxyl groups. Similarly, U.S. Patent Nos. 4,555,559 and 5 4,555,545 (Toshiba Silicone Co.) describe phenolic-functional cyanoacrylates used as stabilizers for polycarbonate resins. U.S. Patent No. 4,576,870 (Rohm GmbH) describes a number of methods of stabilizing polycarbonate resins, including the use of acrylate-functional cyanoacrylates. None of the aforementioned references reveal a means of stabilizing polyurethane or 10 polyester polymers produced by step-growth type polymerizations.

U.S. Patent No. 4,378,194 (General Motors Corp.) describes urethane paints stabilized against UV radiation by copolymerization of hindered piperidinols into the urethane polymer chain. U.S. Patent Nos. 4,831,109 and 4,691,059, assigned to the assignee of the present application, describe 2- 15 hydroxybenzophenone UV radiation stabilizers for polyurethanes, polyesters and polycarbonates in which two or more aliphatic hydroxyl groups are part of an aliphatic chain pendant from one of the aromatic nuclei. Cyanoacrylate UV radiation absorbers are not disclosed in any of these three patents. U.S. Patent No. 5,096,781 (Ciba-Geigy Corp.) discloses unspecified cyanoacrylate-type UV 20 radiation absorbers having at least one quaternary nitrogen moiety in the molecule to impart solubility in water and optionally having from 1 to 3 aliphatic hydroxyl groups in the acrylate ester side chain.

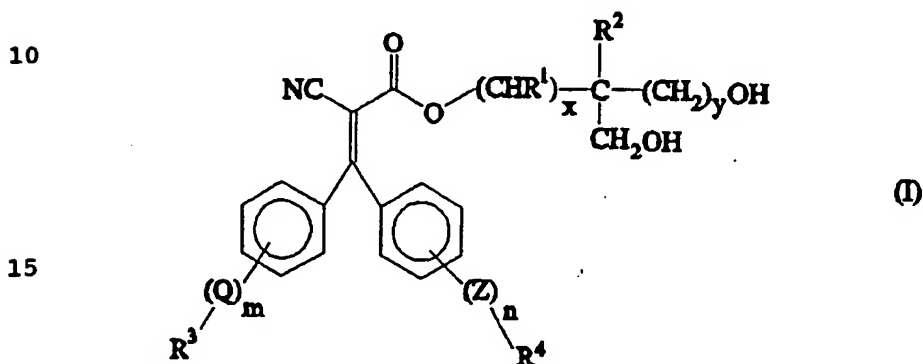
Summary of the Invention

25 A need thus exists for a UV radiation absorber which can be incorporated into a step-growth polymer. None of the cited references describe simple, inexpensive dihydroxy-functional cyanoacrylate-type UV radiation absorbers which can be incorporated directly into step-growth type polymer such as a polyurethane, polyester or polycarbonate main chain by 30 copolymerization so as to impart improved UV radiation resistance to the polymer. I have discovered such a dihydroxy-functional cyanoacrylate UV radiation absorber and polymers which incorporate them.

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The present invention provides for novel hydroxy-functional cyanoacrylate UV radiation absorbing compounds or monomers of formula (I) which are capable of being copolymerized in a step-growth type polymerization reaction to form a UV radiation resistant (co)polymer such as a UV radiation resistant polyurethane, polyester, or polycarbonate polymer.

The copolymerizable hydroxy-functional cyanoacrylate UV radiation absorbing compounds of this invention are exemplified by Formula 1:



20 wherein

R^1 and R^2 are monovalent moieties which can be the same or different and each is independently selected from the group consisting of hydrogen and substituted or unsubstituted alkyl, alkoxyalkyl, aryl, aryloxyalkyl, alkoxyaryl, aralkyl and alkaryl groups, wherein R^1 and R^2 together comprise a total of from about 0 to about 40 carbon atoms or R^1 and R^2 can together form an aliphatic cyclic structure which comprises 5 to 7 carbon atoms and which can optionally further comprise 1 to 2 non-connected oxygen atoms;

x represents an integer of from 0 to about 20;

y represents an integer of 0 to 1; provided that x and y do not simultaneously represent 0; and

R^3 and R^4 are monovalent moieties which can be the same or different and can represent a total of 0 to ten monovalent substituents on the aromatic rings selected from the group consisting of hydrogen; halogen (-Cl, -Br, -F); nitrogen-containing groups selected from the group consisting of nitro, primary amine, secondary amine, tertiary amine, amido, and cyano; substituted or unsubstituted alkyl, aryl, alkenyl, aralkyl, alkoxy, aryloxy, aralkyloxy, alkaryloxy, aryloxyalkyl and thioalkyl moieties comprising from about 1 to

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about 20 carbon atoms and optionally further comprising 1 to about 6 non-connected oxygen and sulfur atoms, wherein said moieties can optionally be substituted by a group selected from the group consisting of halogens and nitrogen-containing groups such as nitro, primary amine, secondary amine, tertiary amine, cyano or amido;

Q and Z are divalent linking species which can be the same or different selected from the group consisting of keto, sulfoxide and sulfone groups;

m is an integer of 0 or 1;

n is an integer of 0 or 1;

The moieties R¹ and R² can each optionally be substituted by a non-proton-donating group (non-nucleophilic group) which preferably is selected from the group consisting of halogen (-Cl, -F, -Br), -NO₂, -CN, an aldehyde group, an acyl group comprising from about 1 to about 10 carbon atoms, and an aroyl group comprising from about 6 to about 10 carbon atoms.

The stabilizer compound of the invention can provide UV radiation resistance to a polymer by reaction into the polymer, typically about 1 to about 7 weight percent of stabilizer compound based upon the total weight of the polymer. Alternatively, the stabilizer compound of the invention can be blended with a polymer, typically about 0.5 to about 10 percent by weight, preferably about 0.5 to about 5 percent by weight of stabilizer compound based upon the total weight of the polymer plus the stabilizer compound.

The invention also provides for polymers in which the compound(s) of formula I are incorporated into the polymer via copolymerization. Examples of such polymers include but are not limited to those selected from the group consisting of polyurethane polymers, polyester polymers, and polycarbonate polymers which have the stabilizer compound of the invention incorporated therein, preferably into the backbone.

The invention also provides for films, webs, sheets, filaments, fibers, coatings, support layers, and cast articles prepared from polymers which incorporate the compounds of formula I.

The following definitions are used herein:

"backbone" means main chain of a polymer, exclusive of pendant or end groups;

"pendant" means suspended from the main chain of a polymer and not an end group;

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"polyester" means a polymer having structural units linked by ester groupings, obtained by condensation of polycarboxylic acids with polyhydric alcohols;

5 "polyurethane" means a polymer characterized by a plurality of urethane groups -NHCOO-;

"polycarbonate" means a polyester of carbonic acid, made by the polymeric condensation of carbonic acid or its derivatives with a polyhydric alcohol;

10 "step growth polymerization" means a multistep reaction for the formation of polymers by chemical reactions such as condensation, addition, and elimination of small molecules;

"cyanoacrylate" means compositions comprising esters of 2-cyano-3,3-diaryl acrylic acid; and

15 "ar" or "aryl" means phenyl, biphenyl, or polynuclear aromatic hydrocarbon groups comprising from about 6 to about 20 carbon atoms and substituted derivatives thereof.

Detailed Description of the Invention

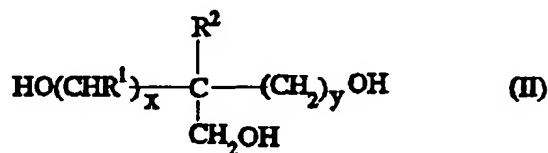
20 The hydroxy-functional cyanoacrylate compound(s) of the invention can be prepared, for instance, by transesterification of a cyanoacrylate ester such as ethyl 3,3-diphenyl-2-cyanoacrylate, available from BASF as UVINUL™ N-35, with a cyclic acetal or ketal of a trihydroxy compound such as glycerol or 2,2-bis(hydroxymethyl)butanol. Acid-catalyzed hydrolysis of the ketal or acetal yields the dihydroxy-substituted cyanoacrylate ester.

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A. Cyclic Acetal

Cyclic acetals useful in the present invention are prepared from the reaction of a trihydroxy compound of the general formula II

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wherein R¹, R², x, and y are as defined above;

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with an aldehyde or ketone of the general formula III

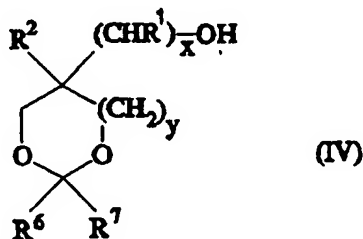


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wherein

R^6 and R^7 are independently selected from the group consisting of H, alkyl, aryl, alkoxyalkyl, aryloxyalkyl, aralkyl, and alkaryl, or R^6 and R^7 together can form an aliphatic cyclic structure comprising from about 5 to about 7 carbon atoms and which can optionally further comprise 1 to 2 non-connected oxygen atoms, wherein together R^6 and R^7 can comprise a total of about 0 to about 40 carbon atoms; in the presence of an acid catalyst to convert the aldehyde or ketone to the cyclic acetal or ketal of the formula IV

15



20

wherein R^1 , R^2 , R^6 , R^7 , x and y are as defined above.

A variety of trihydroxy compounds may be used for this purpose, including but not limited to those selected from the group consisting of glycerol; 2-methylglycerol; 1,2,3-butanetriol; 1,2,4-butanetriol; 1,2,5-pentanetriol; 1,2,6-hexanetriol; 2-methyl-1,2,3-butanetriol; 2-hydroxymethyl-1,3-propanediol; 2-hydroxymethyl-1,3-butanediol; 2-hydroxymethyl-1,4-butanediol; 2-hydroxymethyl-1,5-pentanediol; 2,2-bis(hydroxymethyl)-3-methylhexanol; 2,2-bis(hydroxymethyl)-3-ethylpentanol; 2,2-bis(hydroxymethyl)butanol; 2-hydroxymethyl-2-methyl-1,3-propanediol; 2-hydroxymethyl-2-methyl-1,3-butanediol; 1-phenylglycerol; 2-phenylglycerol; 2-hydroxymethyl-1-phenyl-1,3-propanediol; 2-hydroxymethyl-2-phenyl-1,3-propanediol; and mixtures thereof. Preferably, the triol is selected from the group consisting of glycerol, 2-hydroxymethyl-2-methyl-1,3-propanediol, 2,2-bis(hydroxymethyl)butanol, and mixtures thereof, because of their ease of formation of cyclic acetals or ketals and their commercial availability.

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The aldehyde of the general formula $R^6C(=O)H$, wherein R^6 is as previously defined, needed for preparing the cyclic acetal is preferably selected from the group consisting of formaldehyde, acetaldehyde, propionaldehyde, isobutyraldehyde, chloral, benzaldehyde, o-nitrobenzaldehyde, m-nitrobenzaldehyde, p-nitrobenzaldehyde, m-chlorobenzaldehyde, anisaldehyde, fufural, and mixtures thereof.

To prepare a cyclic ketal, the carbonyl component is a ketone of the general formula $R^6C(=O)R^7$. Preferred ketones according to the present invention are selected from the group consisting of acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclopentanone, cyclohexanone, 3-methylcyclohexanone, acetophenone, benzophenone, and mixtures thereof. Methyl ethyl ketone is the most preferred ketone due to its ready formation of ketals with triols and its facile removal subsequent to ketal hydrolysis.

The method of synthesis of a cyclic acetal or ketal from a 1,2-diol or 1,3-diol and an aldehyde or ketone by acid catalysis is known in the art. The cyclization is usually brought about by treating the hydroxy compound with the aldehyde or ketone in the presence of an acid catalyst such as hydrogen chloride (or hydrochloric acid), sulfuric acid, perchloric acid, p-toluenesulfonic acid, or zinc chloride. The reaction may be carried out in the absence of a solvent, but according to the present invention an inert diluent such as dimethylformamide (DMF), dioxane, ether, benzene, toluene or petroleum ether is preferred. By appropriate choice of this diluent, the water formed in the reaction can be removed by distillation. When the reaction reaches completion, the mixture may be neutralized with a weak base such as sodium acetate and dried with a conventional drying agent such as anhydrous sodium sulfate, before isolating the cyclic acetal or ketal by an isolation method such as one of those known in the art.

B. Cyanoacrylate Ester

Examples of cyanoacrylate ester species which can be reacted with a cyclic acetal or ketal as described above include but are not limited to those selected from the group consisting of ethyl 3,3-diphenyl-2-cyanoacrylate and 2-ethylhexyl 3,3-diphenyl-2-cyanoacrylate, available from BASF as UVINUL™ N-35 and N-539, respectively. These esters are typically produced by the condensation reaction of benzophenone and cyanoacetate esters via the Knoevenagel condensation reaction.

C. Transesterification Reaction

- Cyclic acetals and ketals prepared from trihydroxy compounds, as described above, contain a free primary hydroxyl group. Compounds containing a free primary hydroxyl group will undergo ester exchange or transesterification reactions with a carboxylic ester under conditions in which the newly-formed alcohol moiety is volatile and is removed from the reaction mixture as the reaction progresses (see "Basic Principles of Organic Chemistry", 2nd Edition, J. D. Roberts and M. C. Caserio, W. A. Benjamin, Menlo Park, CA (1977), p. 821).
- Typically, the starting ester is dissolved in a suitable organic solvent and treated with a relatively strong base such as an alkali-metal salt of an alcohol (sodium methoxide, potassium ethoxide, etc.) under reflux in the presence of the new alcohol to be exchanged (in the case of the present invention, the cyclic acetal or ketal bearing a free primary hydroxyl group). Solvent is slowly distilled from the reaction mixture, at which time the more volatile alcohol, initially present in the starting ester, is removed from the reaction concurrent with solvent distillation. Under circumstances where the exchanging alcohol is also somewhat volatile or susceptible to co-distillation, it may be used in large excess to ensure that the ester exchange reaction goes to completion.

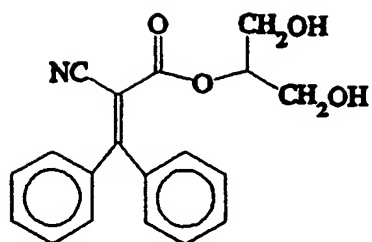
D. Hydrolysis of the Acetal or Ketal

- The cyclic acetal or ketal ester resulting from the above-described ester exchange can now be cleaved by acidic hydrolysis.
- Typically, the acetal or ketal is dissolved in a methanol/water mixture and the pH is adjusted to about pH=1 to about pH=2 by addition of a suitable acid such as hydrochloric acid. Brief heating or refluxing of the mixture results in essentially quantitative cleavage of the cyclic ketal or acetal group to produce the polymerizable dihydroxy compounds of formula (I) of the present invention, which can be isolated by conventional means, including distillation and crystallization techniques.

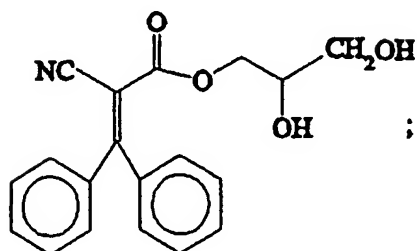
Representative examples of stabilizer dihydroxy compounds of formula (I) include those selected from the group consisting of:

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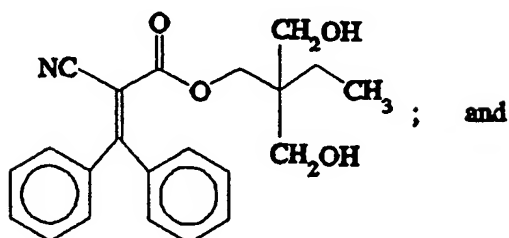
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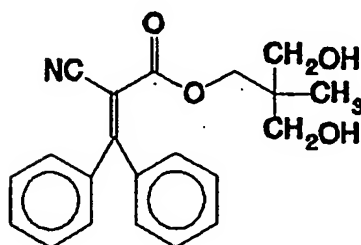


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E. Polymeric Compositions Comprising Dihydroxy Cyanoacrylates Compounds

The dihydroxy ultraviolet stabilizer compound(s) of formula (I) can be incorporated into typical step-growth (co)polymers, e.g., including but not limited to those selected from the group consisting of polyesters, polycarbonates, and polyurethanes. Generally, the stabilizer compound is

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mixed with other polyols such as diols, triols, etc. and cocondensed with compounds selected from the group consisting of dicarboxylic acids including but not limited to those selected from the group consisting of phthalic acid, terephthalic acid, adipic acid, maleic acid, malonic acid, glutaric acid, oxalic acid, succinic acid, malic acid and their esters and their acid chlorides; phosgene; bischloroformates including but not limited to those selected from the group consisting of 1,2-ethanedioldichloroformate, 1,4-butanedioldichloroformate, 1,6-hexanedioldichloroformate, 1,3-dichloroformyloxybenzene, 1,4-dichloroformyloxybenzene, and bisphenol-A-dichloroformate, and mixtures thereof; and diisocyanates including but not limited to those selected from the group consisting of toluene diisocyanate, hexamethylene diisocyanate, and tetramethylene diisocyanate, and mixtures thereof; to produce stabilizer-incorporated polymers. Synthetic techniques for preparing step-growth polymers in general from hydroxy compounds are known in the art and variations of a number of standard methods may be used to prepare the novel polymers of the invention (see "Principles of Polymerization" by G. Odian, 2nd Ed., John Wiley and Sons, N.Y. (1981).

Multifunctional monomers such as those containing acid, acid anhydride, acid chloride ester, and/or isocyanate functionality can undergo condensation polymerization with the ultraviolet stabilizing dihydroxy compounds of the present invention to produce (co)polymers with improved weathering characteristics. The term "multifunctional monomer" as used herein refers to monomers containing two or more functional groups. In addition, mixtures of the compound(s) of formula (I) with other polyhydroxy compound(s) and the multifunctional monomer(s) can undergo polymerization to prepare polyester, polycarbonate, or polyurethane polymers, or mixtures thereof. The ratio of the amounts of stabilizing dihydroxy-functional cyanoacrylate monomer to the amount of added polyol may be varied during polymer syntheses to incorporate different amounts of stabilizing moieties into the (co)polymer. Preferably, about 1% to about 7% by weight of the stabilizing dihydroxy-functional cyanoacrylate compound is incorporated into the final polymer. The copolymers formed may be linear or branched.

A UV radiation stabilized polyester of the present invention can be provided by the reaction of a mixture comprising:

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(a) about 50 mole percent of a dicarboxylic acid selected from the group consisting of aliphatic dicarboxylic acids, aromatic dicarboxylic acids, and mixtures thereof, wherein the dicarboxylic acid comprises from about 2 to about 22 carbon atoms and optionally comprising about 1 to 3 non-
5 connected heteroatoms selected from the group consisting of S, N and O;

(b) about 0 to about 50 mole percent, preferably about 40 to about 49.995 mole percent, of a low molecular weight glycol comprising from about 2 to about 20 carbon atoms, including but not limited to those selected from the group consisting of ethylene glycol, 1,4-butanediol, 1,6-hexanediol,
10 1,4-dimethylolcyclohexane, and dimethylol molecules containing residues selected from the group consisting of aliphatic, aromatic, cycloaliphatic and heterocyclic residues; and

(c) about 0.005 to about 50 mole percent, preferably about 0.005 to about 10 mole percent, of a dihydroxy compound of formula (I);
15 wherein (a), (b), and (c) together comprise 100 mole percent.

A UV radiation stabilized polyurethane according to this invention can be provided by reaction of a mixture comprising:

(a) about 50 mole percent of a diisocyanate selected from the group consisting of aliphatic diisocyanates, aromatic diisocyanates, and mixtures
20 thereof, comprising from about 3 to about 22 carbon atoms and optionally comprising about 1 to about 3 non-connected heteroatoms selected from the group consisting of N, S, and O and combinations thereof;

(b) about 0 to about 50 mole percent, preferably about 40 to about 49.995 mole percent, of a low molecular weight glycol having from
25 about 2 to about 20 carbon atoms, such as ethylene glycol, 1,4-butanediol, 1,6-hexanediol, 1,4-dimethylolcyclohexane, or other dimethylol molecules containing aliphatic, aromatic, cycloaliphatic or heterocyclic residues; and

(c) about 0.005 to about 50 mole percent, preferably about 0.005 to about 10 mole percent, of a dihydroxy compound of formula (I);
30 wherein (a), (b), and (c) together comprise 100 mole percent.

A UV radiation stabilized polycarbonate according to this invention can be provided by reaction of a mixture comprising:

(a) about 50 mole percent of a compound selected from the group consisting of phosgene, an aromatic bis-chloroformate comprising from
35 about 3 to about 22 carbon atoms; an aliphatic bis-chloroformate comprising from about 3 to about 22 carbon atoms; and mixtures thereof;

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(b) about 0 to about 50 mole percent, preferably about 40 to about 49.995 mole percent, of a low molecular weight glycol comprising from about 2 to about 20 carbon atoms, including but not limited to those selected from the group consisting of ethylene glycol, 1,4-butanediol, 1,6-hexanediol, 1,4-dimethylolcyclohexane, or other dimethylol molecules containing aliphatic, aromatic, cycloaliphatic or heterocyclic residues, or a dihydroxy aromatic compound including but not limited to those selected from the group consisting of resorcinol, catechol, hydroquinone, 4,4'-dihydroxybiphenyl, 4,4'-dihydroxydiphenylmethane (bisphenol A), and mixtures thereof; and

(c) about 0.005 to about 50 mole percent, preferably about 0.005 to about 10 mole percent, of a dihydroxy compound of formula (I); wherein (a), (b), and (c) together comprise 100 mole percent.

A catalyst may optionally be used in the preparation of the step-growth polymers having the stabilizing compound of the invention incorporated therein to facilitate the polymerization. Useful catalysts are those typically used to catalyze step growth polymerizations and the amount of catalyst would vary depending upon the polymer to be formed. One skilled in the art would be able to select an appropriate catalyst and amount thereof to facilitate a step growth polymerization. A useful catalyst for preparing a polyester would be a protonic acid or a Lewis acid such as sulfuric acid or zinc chloride. Dibutyltin dilaurate is a useful catalyst for preparing polyurethanes. Useful catalysts for preparing polycarbonates include bases such as pyridine, sodium hydroxide, lithium hydroxide, and the like.

Polymers of the present invention are useful for a number of articles including but not limited to use as fibers, protective films, supports for other materials and as stand alone cast objects and are particularly resistant to UV radiation and sunlight degradation. Polymer films incorporating the polymeric UV radiation stabilizers of this invention show good processability and, when compared with polymers not containing the UV radiation stabilizers in accelerated weathering test, show superior color stability, mechanical performance and reduced crack formation. Polymer films incorporating the hydroxy-functional cyanoacrylate UV radiation absorbing compounds of the invention are also useful as protective elements in layered polymeric film constructions.

The present invention also provides for physical blends of the polymers of the invention with compatible monomers and/or polymers to provide UV stabilized materials.

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The invention will be more fully appreciated with reference to the following non-limiting Examples. All parts, percentages, ratios, etc. in the Examples and the rest of the Specification are by weight unless indicated otherwise.

5

EXAMPLE 1

Ketal Synthesis

A ketal of formula (IV) ($R^1 = H$, $R^2 = R^7 = -CH_2CH_3$, $R^6 = -CH_3$, $x = y = 1$) was prepared as follows: 201 g trimethylolpropane, 216 g methyl ethyl ketone, 3.0 g p-toluenesulfonic acid and 150 g of toluene were heated to reflux and stirred in a 1 liter 3-neck flask equipped with a Dean-Stark water trap, a thermometer and a condenser. After 6 hours of reflux (pot temperature = 95°-105°C), gas chromatographic analysis of the reaction mixture showed that 8% of the triol remained. The reaction mixture was cooled to room temperature, then most of the solvent was removed under aspirator vacuum with heating until the pot temperature reached 100°C. The residual oil was distilled through a short Vigreux column to yield 227 g of a clear liquid, boiling point 105°-115°C at 1.0-1.5 mm Hg.

20

EXAMPLE 2

Dihydroxy-Functional UV Stabilizer Synthesis

A dihydroxy UV radiation stabilizer of formula (I) ($R^1 = R^2 = R^3 = R^4 = H$, $x = 1$, $y = 0$) was prepared as follows: 544 g ethyl 2-cyano-3,3-diphenylacrylate (BASF) was mixed with 2 liters of xylenes in a 5-liter 3-neck flask equipped with a heating mantle, mechanical stirrer, thermometer, addition funnel, Dean-Stark trap and a condenser. Sodium methoxide (1.0 g) was added and the stirred mixture was heated to reflux. A total of 660 g solketal (2,2-dimethyl-1,3-dioxolane-4-methanol, Aldrich) was added dropwise over a 12-hour period. The contents of the Dean-Stark trap were removed periodically and found to be a mixture of solvent and ethanol, the product of the ester exchange reaction. A total of 1500 ml of solvent, ethanol and ketal was removed in this manner, and the removed solvent was replaced with fresh xylenes. The course of the reaction was followed by standard gas chromatographic methods.

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When all of the starting ester had been converted, the solvent was stripped under vacuum and the crude residual oil was taken up in a mixture of 700 ml water and 1500 ml methanol. The stirred solution was treated with

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approximately 15 ml concentrated HCl to bring the pH of the mixture to between 1 and 2, after which the mixture was heated to reflux for two hours. Complete hydrolysis of the ketal was shown by standard gas chromatographic methods and thin layer chromatographic techniques.

- 5 The methanol-water solvent was removed under vacuum and the residue was partitioned between 1 liter of methylene chloride and 1 liter of water containing 50 g sodium bicarbonate. The organic layer was separated and washed twice with 1 liter of water to remove residual methyl ethyl ketone and triol, then dried over anhydrous magnesium sulfate. Removal of the
10 solvent under vacuum gave 550 g of a light yellow oil (85% overall yield). Gas chromatographic analysis showed the oil to be 86% desired diol and 10% of an isomeric dihydroxy diol (formula (I), ($R^1 = R^2 = R_3 = R^4 = -H$, $x = 1$, $y = 0$)), with less than 0.3% residual glycerol.

15 EXAMPLE 3

Dihydroxy-Functional UV Stabilizer Synthesis

- A solution of 276 g ethyl 3,3-diphenyl-2-cyanoacrylate (BASF), 200 g trimethylol propane ketal (prepared according to Example 1) and 5.0 g sodium methoxide in 560 g xylenes was stirred and heated to reflux in a 2-liter
20 3-neck flask equipped with a heating mantle, mechanical stirrer, thermometer, Dean-Stark trap, and condenser. Reflux was continued for 13 hours, with continual removal of ethanol via the trap and replacement of removed xylenes. Gas chromatographic analysis of the reaction mixture showed approximately 95% completion of the transesterification. The mixture was cooled to room
25 temperature and the xylenes were stripped under vacuum while the temperature was kept under 100°C. The residues were treated with 250 ml water, 130 ml methanol and 13.0 g concentrated HCl, and the resultant mixture was refluxed for 5 hours, after which methanol was distilled until the pot temperature reached 100°C. The residue was taken up in 1 liter of isopropyl acetate and
30 washed thoroughly with water. Removal of isopropyl acetate gave 336 g dense white solid. Gas chromatographic analysis showed the solid to be 97% pure, with less than 0.2% residual triol. A C^{13} NMR spectrum of the product confirmed the structure as formula I ($R_1 = R_3 = R_4 = -H$, $R_2 = -C_2H_5$, $x = y = 1$).

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EXAMPLE 4

Polyester Polyurethane Urea Containing Dihydroxy-Functional UV Stabilizer

A solution of 177.92 g Ruco S-1035-110 Polyester (a mixed aliphatic/aromatic polyester polyol, number average molecular weight approximately 1000, from Ruco Polymer Corp.), 27.04 g dimethylol propionic acid (DMPA), 163.64 g hydrogenated diphenylmethane diisocyanate (H_{12} MDI), 16.68 g dihydroxy-functional UV stabilizer of Example 3 (4.1% by total weight of polyester, diisocyanate and UV stabilizer) and 2 drops of dibutyltin dilaurate in 148.74 g methyl ethyl ketone (MEK) was stirred and heated to reflux for three hours to obtain a polyurethane prepolymer. A total of 200 g of the prepolymer was then treated with 380 g chilled deionized water, 7.35 g triethylamine and 6.16 g 1,3-diaminopentane (DAMP) in a Gifford-Wood mixer to obtain a translucent bluish emulsion. Excess MEK was removed under vacuum to obtain a polyurethane coating material containing 36.6% solids and a Brookfield viscosity of 728 cps.

EXAMPLE 5

Weathering of Polymers

The waterborne polyester polyurethane urea of Example 4 was bar-coated onto an industry-standard automobile paint sample (a two-part urethane paint) on an automobile steel panel which was subsequently dried in an oven at 100° C for 5 minutes then at 200° C for one minute. The samples were exposed to both outdoor and accelerated weathering along with control samples. Control samples comprised the polyester polyurethane urea clear coat with no copolymerized UV radiation absorbing compound therein.

Outdoor weathering tests were conducted according to ASTM G-7 methods (Annual Book of ASTM Standards, Vol. 6.01). Test panels measuring 11 x 28 cm were mounted in racks facing south at 5° (Florida) and 45° (Arizona) from horizontal and exposed to direct weathering for 24 months. Evaluation of samples and controls was by visual inspection, at 12-month intervals.

Indoor accelerated weathering tests were conducted according to ASTM G-23, Type E methods (Annual Book of ASTM Standards, Vol. 6.01). Test panels measuring 11 x 11 cm were mounted in an Atlas Electric Devices open flame carbon arc (filtered by Corex D glass panes) weatherometer, model XW and exposed to cycles of 102 minutes of light at 63° C (black panel) followed by 18 minutes of light plus water spray, for a total of 1000 hours.

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Samples were also tested by exposure in an Atlas Electric Devices twin enclosed carbon arc (filtered by 9200-PX borosilicate globes) weatherometer, model DMC, under the above conditions and time. In a third test, panels were exposed to a single carbon arc filtered by a 9200-PX borosilicate globe in an
5 Atlas Electric Devices Fade-O-Meter™ weatherometer under continuous light at 63° C (black panel) for 1000 hours.

Comparison of test panels to controls, when tested under each of the conditions noted above, showed that paint samples protected with a clear coating of the waterborne polyester polyurethane of Example 4 containing 4.1%
10 of the hydroxyfunctional cyanoacrylate UV radiation absorbing compound of Example 3 exhibited noticeably less yellowing and fewer cracks as compared to the control samples.

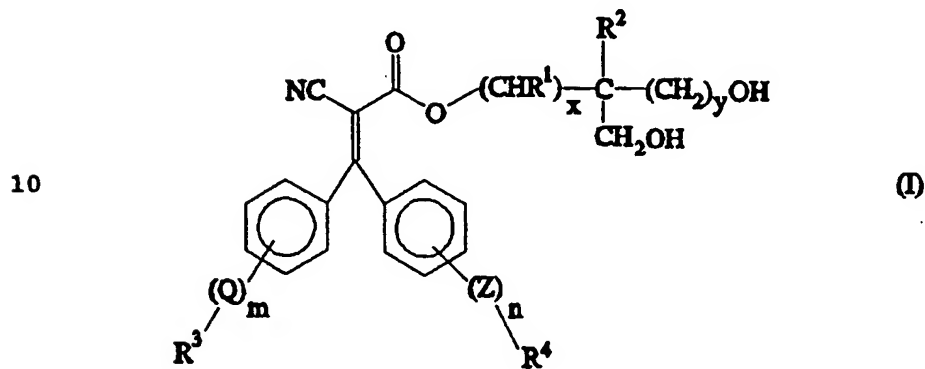
While this invention has been described in connection with specific embodiments, it should be understood that it is capable of further
15 modification. The claims herein are intended to cover those variations which one skilled in the art would recognize as the chemical equivalent of what has been described herein.

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CLAIMS

1. An ultraviolet radiation absorbing compound comprising a compound of the formula I

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wherein

R_1 and R_2 are the same or different and each is selected from the group consisting of hydrogen and substituted or unsubstituted alkyl, alkoxyalkyl, aryl, aryloxyalkyl, alkoxyaryl, aralkyl, and alkaryl groups, or R_1 and R_2 together form an aliphatic cyclic structure which comprises 5 to 7 carbon atoms and which can optionally further comprise 1 to 2 non-connected oxygen atoms, wherein R_1 and R_2 together can comprise a total of from 0 to about 40 carbon atoms;

x represents an integer of from 0 to about 20;

y represents an integer of 0 to 1; provided that x and y do not simultaneously represent 0; and

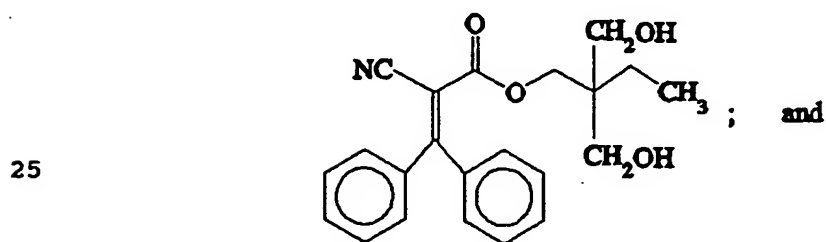
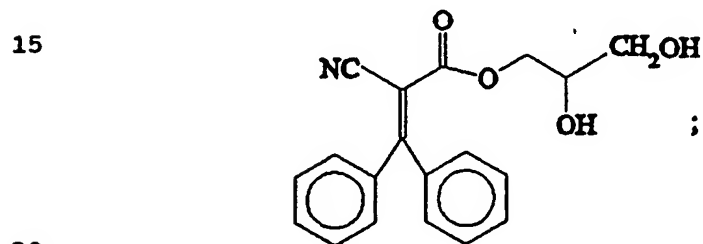
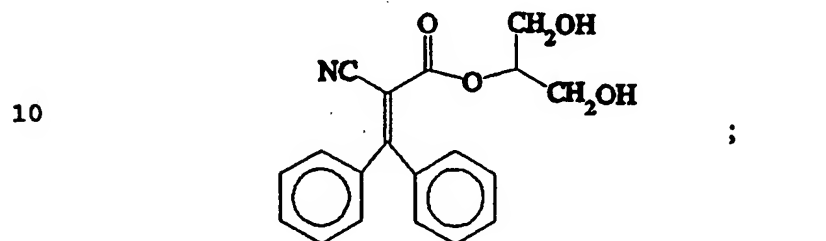
R_3 and R_4 are monovalent moieties which can be the same or different and represent a total of 0 to 10 monovalent substituents on the aromatic rings selected from the group consisting of hydrogen; halogen nitrogen-containing groups; substituted or unsubstituted alkyl, aryl, alkenyl, aralkyl, alkoxy, aryloxy, aralkyloxy, alkaryloxy, aryloxyalkyl and thioalkyl moieties comprising from about 1 to about 20 carbon atoms and optionally further comprising about 1 to about 6 non-connected oxygen and sulfur atoms, wherein said moieties can optionally be substituted by halogen or a nitrogen-containing group;

Q and Z are divalent linking species which can be the same or different selected from the group consisting of keto, sulfoxide, and sulfone groups;

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m represents an integer of 0 or 1; and
n represents an integer of 0 or 1.

2. The ultraviolet radiation absorbing compound of Claim 1 wherein
5 said compound is selected from the group consisting of:

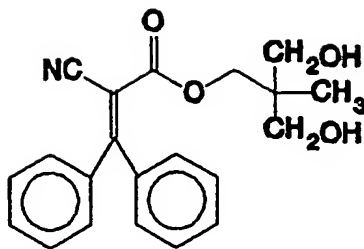


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10 3. A UV radiation stabilized material comprising a polymer having the ultraviolet radiation absorbing compound of Claim 1 incorporated therein.

4. A UV radiation stabilized material comprising a polyester having the ultraviolet radiation absorbing compound of Claim 1 incorporated therein.

15 5. A UV radiation stabilized material comprising a polyurethane having the compound of Claim 1 incorporated therein.

20 6. A UV radiation stabilized material comprising a polycarbonate having the compound of Claim 1 incorporated therein.

7. An ultraviolet radiation stabilized polyester comprising the reaction product of:

- (a) about 50 mole percent of a dicarboxylic acid;
- (b) about 0 to about 50 mole percent of a glycol comprising
- 25 from about 2 to about 20 carbon atoms; and
- (c) about 0.005 to about 50 mole percent of the dihydroxy compound of Claim 1;

wherein (a), (b), and (c) together comprises 100 mole percent.

30 8. An ultraviolet radiation stabilized polyurethane comprising the reaction product of:

- (a) about 50 mole percent of a diisocyanate;
- (b) about 0 to about 50 mole percent of a glycol comprising
- from about 2 to about 20 carbon atoms; and

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(c) about 0.005 to about 50 mole percent of the dihydroxy compound of Claim 1;
wherein (a), (b), and (c) together comprises 100 mole percent.

5 9. An ultraviolet radiation stabilized polycarbonate comprising the reaction product of:

 (a) about 50 mole percent of a compound selected from the group consisting of phosgene, an aromatic bis-chloroformate comprising from about 3 to about 22 carbon atoms; an aliphatic bis-chloroformate comprising
10 from about 3 to about 22 carbon atoms; and mixtures thereof;

 (b) about 0 to about 50 mole percent glycol comprising from about 2 to about 20 carbon atoms; dimethylol molecules containing aliphatic, aromatic, cycloaliphatic or heterocyclic residues; dihydroxy aromatic compounds; and mixtures thereof; and

15 (c) about 0.005 to about 50 mole percent of the compound of Claim 1;


 wherein (a), (b), and (c) together comprise 100 mole percent.

20 10. An article comprising the polymer of Claim 3.

 11. An article selected from the group consisting of fibers, protective films, supports, and cast objects, comprising the polymer of Claim 3.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 93/12260

A. CLASSIFICATION OF SUBJECT MATTER		
IPC5: C07C 255/41, C08G 18/38, C08G 63/193, C08G 64/16 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
IPC5: C07C		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
REG		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP, A1, 0017703 (GAF CORPORATION), 29 October 1980 (29.10.80) --	1-3,5,8, 10-11
X	US, A, 4129667 (DONALD H. LORENZ ET AL.), 12 December 1978 (12.12.78) --	1-4,7,10-11
X	US, A, 4202834 (BRUCE A. GRUBER ET AL.), 13 May 1980 (13.05.80) --	1-4,7,10-11
X	US, A, 4218392 (DONALD H. LORENZ ET AL.), 19 August 1980 (19.08.80) --	1-4,7,10-11
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
28 March 1994		14. 04. 94
Name and mailing address of the International Searching Authority/Authorized officer		
 European Patent Office, P.B. 5818 Patendaan 2 NL-2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		IRJA BERLIN

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 93/12260

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 4247475 (TA-YEN CHING), 27 January 1981 (27.01.81) --	1-3,6,9-11
X	US, A, 4366207 (BLAIR T. ANTHONY), 28 December 1982 (28.12.82) --	1-3,6,9-11
X	US, A, 4555545 (HIROSHI KIMURA ET AL.), 26 November 1985 (26.11.85) --	1-3,6,9-11
X	US, A, 4555559 (HIROSHI KIMURA ET AL.), 26 November 1985 (26.11.85) -- -----	1-3,6,9-11

INTERNATIONAL SEARCH REPORT

Information on patent family members

26/02/94

International application No.

PCT/US 93/12260

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A1- 0017703	29/10/80	AU-A- 5303579	31/07/80
		JP-A- 55100351	31/07/80
		US-A- 4178303	11/12/79
		US-A- 4207253	10/06/80
		US-A- 4218392	19/08/80
		US-A- 4263366	21/04/81
		US-A- 4276136	30/06/81
		US-A- 4202836	13/05/80
		US-A- 4202834	13/05/80
		US-A- 4203919	20/05/80
US-A- 4129667	12/12/78	CA-A- 1106525	04/08/81
		EP-A- 0002676	11/07/79
		JP-A- 54106543	21/08/79
		US-A- 4216267	05/08/80
US-A- 4202834	13/05/80	AU-A- 5303579	31/07/80
		EP-A- 0017703	29/10/80
US-A- 4218392	19/08/80	AU-A- 5303579	31/07/80
		EP-A- 0017703	29/10/80
		JP-A- 55100351	31/07/80
		US-A- 4178303	11/12/79
		US-A- 4207253	10/06/80
		US-A- 4263366	21/04/81
		US-A- 4276136	30/06/81
US-A- 4247475	27/01/81	CA-A- 1164886	03/04/84
		DE-A, C- 3106071	18/02/82
		JP-C- 1590944	30/11/90
		JP-B- 2017538	20/04/90
		JP-A- 56140959	04/11/81
US-A- 4366207	28/12/82	EP-A, B- 0093968	16/11/83
		JP-A- 58217548	17/12/83
US-A- 4555545	26/11/85	JP-A- 60166355	29/08/85
US-A- 4555559	26/11/85	JP-C- 1694043	17/09/92
		JP-B- 3062177	25/09/91
		JP-A- 60166327	29/08/85